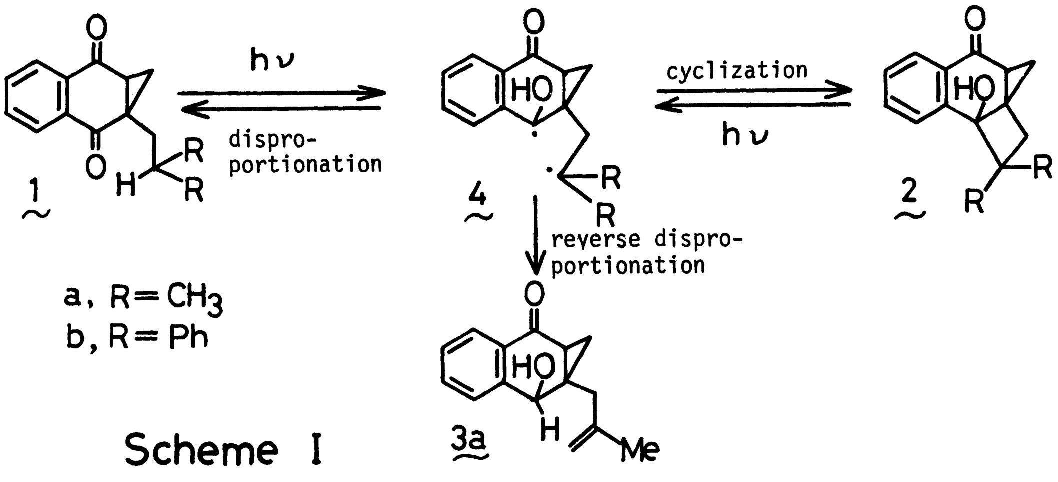
CHEMISTRY LETTERS, pp. 329-332, 1982.

MONORADICAL REARRANGEMENT OF 1,4-BIRADICALS INVOLVED IN NORRISH TYPE II PHOTOREACTION OF METHANONAPHTHOQUINONES

Atsuhiro OSUKA,* Hirohito SHIMIZU, and Hitomi SUZUKI
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790
Kazuhiro MARUYAMA
Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

Type II photoreaction of the title compound gave a cyclobutanol by cyclization, an unsaturated keto alcohol by reverse disproportionation, and a bicyclic diketone by cyclopropylcarbinyl rearrangement. Relative rates of the type II biradical reactions were estimated on the basis of the product analysis.

Considerable attention has been focused in recent years on monoradical reactions of the 1,4-biradicals involved in Norrish type II reaction.[1] However, studies have been rather limited to the reactions at alkyl radical sites, because alkyl radical is much more reactive than ketyl radical. In a recent publication, we reported that type II biradical 4 are formed on excitation of the cyclobutanol 2a as well as by the normal type II pathway from 1a and finally collapses to the unsaturated keto alcohol 3a by reverse disproportionation.[2] In type II biradicals, reverse disproportionation is very



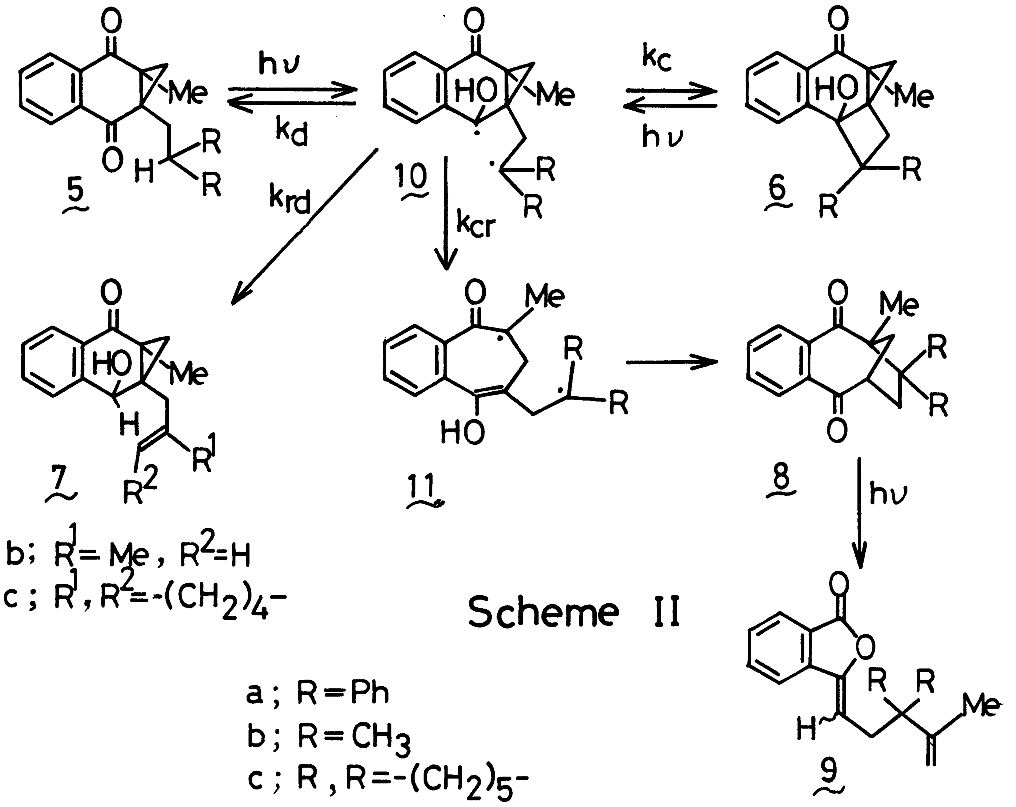
Scheme I

rare, since it cannot compete with usual type II processes such as disproportionation, cyclization, and elimination.[3,4] Absence of products derived from the opening of the three-membered ring indicated that cyclopropyl carbinyl rearrangement is yet slower than reverse disproportionation. We now describe some experiments demonstrating that cyclopropylcarbinyl rearrangement at ketyl radical site becomes important by introduction of methyl group at the three-membered ring.

Irradiation of 2-(2,2-diphenyl)ethyl-2,3-dihydro-2,3-methano-1,4-naphthoquinone (1b)(0.02 M) in benzene with a 300W high-pressure Hg lamp through a Pyrex filter under an argon atmosphere for 5 h furnished a 1:4 mixture of the cyclobutanol 2b and 1b. Extended irradiation of this mixture did not enhance the degree of conversion. Then, separation of the products by column chromatography over silica gel gave 2b in 53% yield.[5] A separate irradiation of 2b in benzene also led to the same mixture of 2b and 1b, indicating that the photoequilibrium between 2b and 1b was attained with 4b as a common intermediate. The ratio of 2b to 1b increases significantly with added alcohol; 2b/1b is 4 in benzene-Bu^tOH (1:1).

In contrast, irradiation of 2-methyl-3-(2,2-diphenyl)ethyl-2,3-dihydro-2,3-methano-1,4-naphthoquinone (5a) in benzene for 30 h gave exclusively rise to a bicyclic diketone 8a in 83% yield. In this case, the formation of the corresponding cyclobutanol 6a was not detected during the course of the reaction. The structure of 8a was assigned on the basis of its spectral data and elemental analysis. The IR spectrum of 8a showed characteristic bands at 1695 and 1665 (conjugated ketones) cm^{-1}; the ^1H-NMR ($CDCl_3$) spectrum showed the signals at 1.18(s, Me), 2.28(d, J=15Hz, 1H), 2.60(dd, J=8 and 15Hz, 1H), 2.88(dd, J=4 and 16Hz, 1H), 3.42(dd, J=10 and 16Hz, 1H), and 3.62(m, 1H), indicating the presence of $-CH_2-CH-CH_2-$ group; ^{13}C-NMR ($CDCl_3$) spectrum revealed the presence of two ketones at 204.4 and 199.2, two quaternary carbons at 63.9 and 60.7, one methine carbon at 50.2, two methylene carbons at 45.2 and 42.1, and methyl carbon at 22.7, besides aromatic carbons. As shown in Scheme II, the formation of 8a can be best explained by a mechanism involving cyclopropylcarbinyl rearrangement of type II biradical 10a to 11a followed by radical recombination. Radical center α to carbonyl group in 11a would be better stabilized by methyl group.

Upon irradiation in benzene-Bu^tOH (1:1) for 5 h, 2-methyl-3-(2-methyl)propyl-2,3-dihydro-2,3-methano-1,4-naphthoquinone (5b)gave the cyclobutanol 6b (17%),[5] the unsaturated keto alcohol 7b (11%),[5] the bicyclic diketone 8b (30%),[5] and the alkylidene phthalide 9b (9%).[5] The last compound is secondary photoproduct derived from 8b. In fact, exposure of 8b under the same irradiation conditions readily produced 9b.[6] It is of



Scheme II

mechanistic interest to estimate the relative rates of reverse disproportionation (k_{rd}) and cyclopropyl carbinyl rearrangement at the ketyl radical site (k_{cr}) to the usual type II biradical reaction such as disproportionation (k_d) or cyclization (k_c). For this purpose, the cyclobutanol 6b is a favorable precursor of type II biradical 10b, since photochemical production of 10b from 6b in benzene is about 27.5 times as efficient as the apparent disappearance of 5b by the usual type II pathway[7]. On photolysis, 6b afforded 5b, 7b, and 8b in the ratio of 170:1:4.6, reflecting the relative rates of k_d:k_{rd}:k_{cr} in 10b. Taking the photolability of 8b into account, the ratio of k_{cr}/k_{rd}(4.6) agreed well with the product ratio of 8b+9b/7b (3.5) in the photolysis of 5b. Similar irradiation of 6b in methanol gave 5b, 7b, and 8b in the ratio of 9.5:1:4.5. It is interesting to note that disproportionation is suppressed only incompletely even in methanol. We suppose that steric hindrance around the hydroxyl group in 10b prevents the biradical solvation by alcohol. On the other hand, the cyclohexyl-substituted compound 5c furnished on photolysis the cyclobutanol 6c (61%), the unsaturated keto alcohol 7c (8%), and the alkylidene phthalide 9c (2%) in benzene-$\mathrm{Bu^tOH}$ (1:1). Irradiation of 6c in benzene gave 5c, 7c, and 8c in the ration of 50:1.5:1. Consequently, the cyclopropyl carbinyl rearrangement is of minor importance in 10c, presumably because of rather efficient reverse disproportionation.

References

1, a), M. V. Encinas, P. J. Wagner, and J. C. Scaiano, J. Am. Chem. Soc., 102, 1357 (1980). b), P. J. Wagner, K-C. Liu, and Y. Noguchi, J. Am. Chem. Soc., 103, 3837 (1981). c), P. J. Wagner, M. J. Lindsrom, J. H. Sedon, and D. R. Ward, ibid., 103, 3842 (1981). d), P. J. Wagner, "Photorearrangements via Biradicals of Simple Carbonyl Compounds", ed by P. de Mayo, Academic Press, New York (1980), p.p. 381-444.

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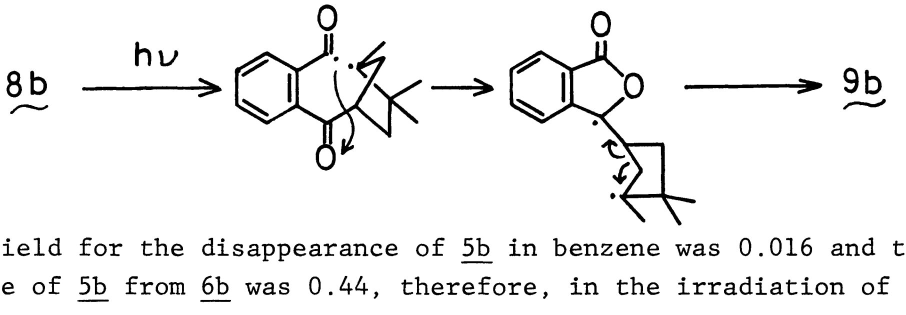
3, 4-Cycloundecenol was reported to be formed in 8% yield in the photochemical reaction of cycloundecanone in benzene; K. Matsui, T. Mori, and H. Nozaki, Bull. Chem. Soc. Jpn., 44, 3440 (1971). To our knowledge, this is the only reported case of reverse disproportionation in type II biradicals.

4, P. J. Wagner, Acc. Chem. Res., 4, 168 (1971).

5, All new compounds gave satisfactory elemental analyses and spectral data. Selected physical properties follow. 2b; mp 144-146°C; IR (KBr) 3370(OH) and 1640(a conjugated C=O) cm^{-1}; ^{1}H-NMR(CDCl$_3$) 1.1(m, 1H), 1.4(m, 1H), 2.07(dd, J=6 and 9Hz, 1H), 3.20 and 3.64(ABq, J=12Hz, 2H), and 7.1-8.0(m, 14H); ^{13}C-NMR(CDCl$_3$) 195.0(s), 81.0(s), 64.0(s), 38.3(s), 30.0(t), 29.7(d), 12.8(t). 6b; mp 110.5-111°C; IR(KBr) 3450(OH), 1650(C=O), 1600, and 750 cm^{-1}; ^{1}H-NMR(CDCl$_3$) 0.82(s, Me), 1.30(s, Me), 1.34(s, Me), 0.80 and 1.17(ABq, J=6Hz, 2H), 1.81 and 2.59(ABq, J=11Hz, 2H), 7.1-7.5(m, 3H), and 7.8-8.1(m, 1H). 7b; colorless oil; IR(CCl$_4$) 3400(OH), 1640(C=O), and 1600 cm^{-1}; ^{1}H-NMR(CDCl$_3$)0.84 and 1.25(ABq, J=5Hz, 2H), 1.47(s, Me), 1.80(s, -C=C-Me), 2.06 and 3.01(ABq, J=16Hz, 2H), 4.85(m, -C=CH$_2$), 5.07(s, 1H), and 7.0-7.9(m, 4H). 8b; mp 53-54°C; IR(KBr) 1680(C=O), 1660(C=O), and 1595 cm^{-1}; ^{1}H-NMR(CDCl$_3$) 0.98(s, Me), 1.07 (s, Me), 1.23(s, Me), 1.6-2.4(m, 4H), 3.4(m, 1H), 7.6-7.7(m, 2H), 8.0-8.2(m, 2H); ^{13}C-NMR(CDCl$_3$)205.4(s), 201.3(s), 47.5(d), 45.1(s), 44.0(t), 38.3(t), 29.8(s), 26.5 (q), 24.5(q), and 18.8(q). 9b;mp 38-39°C; IR(KBr) 2960, 1770(phthalide C=O), and 985 cm^{-1}; ^{1}H-NMR(CDCl$_3$)1.13(s, 6H), 1.77(s, -C=C-Me), 2.51(d, J=8Hz, -C=C-CH$_2$-), 4.70(s, -C=CH$_2$), 5.32(t, J=8Hz, 1H), and 7.3-7.8(m,4H); the stereochemistry around the double bond was not determined yet.

6, Photorearrangement of 8b to 9b might proceed via α-cleavege followed by radical rearrangement; K. Maruyama, A. Osuka, and H. Suzuki, Chem. Lett., 1979, 1477.



7, Quantum yield for the disappearance of 5b in benzene was 0.016 and that for the appearance of 5b from 6b was 0.44, therefore, in the irradiation of 6b, the secondary type II photoreaction can be safely neglected.

(Received November 19, 1981)